

PART ONE
THE STRUCTURE OF CYCLIC TERTIARY VINYL
AMINES

PART TWO
RESTRICTED ROTATION IN NAPHTHYLAMINES

BY
RAYMOND HARDING MATTSON

B.S., University of Michigan, 1943

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1951

URBANA, ILLINOIS

1951

PART ONE
THE STRUCTURE OF CYCLIC TERTIARY VINYL
AMINES

PART TWO
RESTRICTED ROTATION IN NAPHTHYLAMINES

BY
RAYMOND HARDING MATTSON

B.S., University of Michigan, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1951

URBANA, ILLINOIS

1951

ACKNOWLEDGMENT

The author wishes to express his gratitude to Professor Roger Adams for his guidance and encouragement during the investigation of these problems, and to all the members of the Chemistry Faculty whose opinions were frequently sought.

Further, the author is indebted to the University of Illinois for an assistantship during 1946 - 1947 and to the Eastman Kodak Company for fellowships during 1947 - 1949.



PART ONE

THE STRUCTURE OF CYCLIC TERTIARY VINYL AMINES

INTRODUCTION

Tertiary vinyl amines are stronger bases than the corresponding saturated analogues, whereas the primary and secondary vinyl amines are weaker bases than their saturated counterparts. To explain this, it has been suggested (1) that the double bond of tertiary vinyl amines is capable of shifting, in the presence of acids, including water, to form quarternary ammonium compounds, the hydroxides of which are known to be strong bases.

It was the purpose of this research to synthesize members of this unusual class of amines and to seek evidence of such a double bond migration.

DISCUSSION OF RESULTS

Only one member of the tertiary vinyl amines, 1,2-dimethyl-3-phenyl- Δ^2 -tetrahydropyridine, was synthesized. It was obtained *via* the sequence: phenyl acetone, 3-phenyl-6-ethoxyhexan-2-one, 3-phenyl-6-bromohexan-2-one, 1,2-dimethyl-3-phenyl- Δ^2 -tetrahydropyridine. The synthesis was first attempted by a route which involved the ethanolysis of α -phenylacetone to ethyl α -phenylacetate according to an established procedure (2). The synthesis of the latter compound was attempted twice and both times the major product was α -phenyl- β -ethoxycrotononitrile, the structure of which was determined by infrared absorption spectrum and elementary analysis.

In 50 per cent aqueous methanol, the tertiary vinyl amine was found to be more basic than 1,2-dimethyl-3-phenylpiperidine by approximately one pK_H unit, but the former proved to be too unstable for reproducible ultraviolet absorp-

tion spectra, and no conclusions could be drawn as to the position of the double bond in question.

The syntheses of 1,2-dimethyl-3-benzyl- Δ^2 -tetrahydropyridine and 1,2,3-trimethyl- Δ^2 -tetrahydropyridine were also attempted, but synthetic difficulties prevented their realization.

A survey of the literature on vinyl amines and factors affecting basicity, notably resonance and steric hindrance, led to the suggestion that the high basicity of tertiary vinyl amines arises as a result of hydrolysis to the corresponding secondary amine and aldehyde or ketone, and that hydrogen bonding may operate to enhance the basicity of the hydrolytic products above that of ordinary secondary amines.

BIBLIOGRAPHY

1. Adams and Mahan, J. Am. Chem. Soc., 64, 2588 (1942).
2. Kimball, Jefferson and Pike, "Organic Syntheses", Coll. Vol. II, John Wiley and Sons, Inc., New York, 1943, p. 284.

PART TWO

RESTRICTED ROTATION IN NAPHTHYLAMINES

INTRODUCTION

Kuhn and Albrecht (1), in their studies of restricted rotation in the biphenyl series, were the first to show that stereochemical stability is subject to the influence of substituents in non-interfering positions of the molecule. Later, the work of Adams and Sundholm (2) demonstrated that the phenomenon was also present in the aryl amine series of restricted rotation isomers. Thus, the half-life of optical activity of N-succinyl-1-methylamino-2,4-dimethyl-6-bromobenzene in boiling *n*-butanol was found to be three and one-tenth hours in contrast to one

and one-tenth hours under the same conditions for N-succinyl-1-methylamino-2-methyl-4,6-dibromobenzene. To account for this anomaly, Adams and Sundholm (loc. cit) suggested that the presence of electronegative groups in the aromatic nucleus enhances the amount of double bond character associated with the linkage joining the amino nitrogen to the ring carbon, which means an increased tendency toward coplanarity of the ring and the two remaining amino nitrogen bonds. Since racemization must take place through a coplanar constellation, it was held that an increase in double bond character of the ring to nitrogen bond resulted in an increase in rate of racemization.

Subsequent researches have been more or less consistent with the foregoing hypothesis, and it was the object of this work to determine the effect on constellational stability of substituents in the 4 position of the naphthalene nucleus of N-benzenesulfonyl-N-carboxymethyl-1-amino-2-methylnaphthalene.

DISCUSSION OF RESULTS

Three compounds of the series, the 4-chloro, the 4-bromo and the parent compound, were prepared and resolved through the cinchonine salts. To obtain the first of these, 1-nitro-2-methylnaphthalene was converted, by the method of Adams and Albert (3), to 1-amino-2-methyl-4-chloronaphthalene which was then treated successively with benzenesulfonyl chloride, ethyl bromoacetate, and dilute sulfuric acid to give *dl*-N-benzenesulfonyl-N-carboxymethyl-1-amino-2-methyl-4-chloronaphthalene. The other two *dl*-acids were prepared from the corresponding amines in the same way. Catalytic reduction of 1-nitro-2-methylnaphthalene gave 1-amino-2-methylnaphthalene, and part of this was acetylated, brominated, and hydrolyzed to yield 1-amino-2-methyl-4-bromonaphthalene. Attempts to prepare the 4-nitro member of the series by a similar route were unsuccessful, because suitable conditions were not found for the benzenesulfonation of 1-amino-2-methyl-4-nitronaphthalene.

Separation of the diastereomeric cinchonine salts was complicated by the fact that the specific rotations of successive crops of crystals were erratic. It was necessary finally to combine the fractions according to specific rotation and recrystallize the combined fractions to constant rotation.

The half-life of optical activity of these compounds in boiling *n*-butanol was determined and found to be four hours for the 4-chloro acid, three and seven-tenths hours for the 4-bromo analogue and three and one-half hours for the parent compound. In view of the small differences involved, it is believed that these data are inconclusive, and that more evidence is needed before a theory of racemization for this series can be advanced on a sound basis.

A review of some of the literature on restricted rotation indicates that the same concept of double bond character at the site of restricted rotation is applicable in the biphenyl series and that the observations in the two series are not incompatible as had been previously supposed.

In the course of attempts to obtain N-benzenesulfonyl-1-amino-2-methyl-4-nitronaphthalene it was shown that treatment of N-benzenesulfonyl-1-amino-2-methylnaphthalene with a mixture of concentrated nitric acid and glacial acetic acid at about 85° results in N-benzensulfonyl-1-amino-2-methyl-4-nitronaphthalene. To establish the location of the nitro group, the latter was reduced and the amine benzenesulfonated to give N,N'-dibenzenesulfonyl-1,4-diamino-2-methylnaphthalene. The melting point of an intimate mixture of this product and an authentic sample prepared from 1-amino-2-methyl-4-nitronaphthalene, a known compound, showed no depression.

BIBLIOGRAPHY

1. Kuhn and Albrecht, *Ann.*, 458, 221 (1927).
2. Adams and Sundholm, *J. Am. Chem. Soc.*, 70, 2667 (1948).
3. Adams and Albert, *ibid.*, 64, 1475 (1942).

VITA

The author was born in Matchwood, Michigan on October 10, 1920 and attended public schools in Ontonagon and Gogebic Counties. He was graduated from the Wakefield High School in 1937 and two years later entered the University of Michigan. The degree of Bachelor of Science in Chemistry was conferred upon him by that institution in February, 1943, after which he was employed by the Rohm and Haas Company of Philadelphia, Pennsylvania. During the winter of 1943-1944 he attended night classes in organic chemistry at Temple University. His employment with Rohm and Haas terminated in July, 1944 when he entered the United States Naval Reserve as an ensign. His military Service included duty aboard a fleet oiler, training in Russian at the Naval Training School of Oriental Languages at Boulder, Colorado and assignment in the Department of Naval Intelligence in Washington, D.C. In 1946 he was released from active duty and entered the Graduate College of the University of Illinois in September of that year. He held an assistantship in organic chemistry during the academic year of 1946-1947 and during the succeeding two years held an Eastman Kodak Fellowship.



Digitized by the Internet Archive
in 2026

